



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 170 388 A1**

(12)

**EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 158(3) EPC

(43) Date of publication:  
09.01.2002 Bulletin 2002/02

(21) Application number: 00981824.6

(22) Date of filing: 19.12.2000

(51) Int Cl.<sup>7</sup>: **C21D 9/46**, C22C 38/00,  
C22C 38/06, C22C 38/12,  
H01J 29/07

(86) International application number:  
PCT/JP00/08984

(87) International publication number:  
WO 01/46480 (28.06.2001 Gazette 2001/26)

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE TR

(30) Priority: 20.12.1999 JP 36069799

(71) Applicant: NKK CORPORATION  
Tokyo 100-0005 (JP)

(72) Inventors:  
• KODAMA, Satoshi NKK Corporation  
Tokyo 100-0005 (JP)  
• SUGIHARA, Reiko NKK Corporation  
Tokyo 100-0005 (JP)

- MATSUOKA, Hideki NKK Corporation  
Tokyo 100-0005 (JP)
- TAMAKA, Yasushi NKK Corporation  
Tokyo 100-0005 (JP)
- HIRATANI, Tatsuhiko NKK Corporation  
Tokyo 100-0005 (JP)
- TAHARA, Kenji NKK Corporation  
Tokyo 100-0005 (JP)
- MITSUZUKA, Kenichi NKK Corporation  
Tokyo 100-0005 (JP)

(74) Representative: HOFFMANN - EITLE  
Patent- und Rechtsanwälte Arabellastrasse 4  
81925 München (DE)

(54) **STEEL SHEET FOR TENSION MASK, METHOD FOR PRODUCING THE SAME AND TENSION MASK**

(57) The present invention relates to a method of making a steel sheet for a tension mask, comprising the steps of: hot rolling a steel containing, by weight %, C: less than 0.1 %, Si: 0.05 % or less, Mn: 0.4 to 2 %, P: 0.03 % or less, S: 0.03 % or less, sol.Al: 0.01 % or less, N: 0.010 % or more, and the balance being substantially Fe; cold rolling the hot rolled steel sheet; and annealing

the cold rolled steel sheet, followed by a secondary cold rolling at a reduction rate of 35 % or higher. The steel sheet produced by this method shows excellent creep resistance during blackening treatment and excellent magnetic shielding property with an anhyseretic permeability of 3400 or more at a DC bias magnetic field of 0.35 Oe, and therefore causes no color-deviation when applied to the tension mask.

EP 1 170 388 A1

## Description

## TECHNICAL FIELD

- 5 [0001] The present invention relates to a steel sheet for a tension mask incorporated in color cathode ray tubes of televisions or computers, a making method thereof, and a tension mask using the same.

## BACKGROUND OF THE INVENTION

- 10 [0002] Some color cathode ray tubes of televisions or computers incorporate a color selection electrode loaded with large tension like an aperture grill as a color selection mechanism, so-called a tension mask.
- [0003] The tension mask is in general produced by subjecting a low carbon steel or an ultra low carbon Al-killed steel to hot rolling, cold rolling, continuous annealing, secondary cold rolling, and, as needed, to annealing for removing residual stress, followed by making apertures by photo-etching process, attaching to a frame by loading a tension of
- 15 200 to 400 N/mm<sup>2</sup>, for example, in one direction or two directions, and performing blackening treatment.
- [0004] The blackening treatment is a heat treatment heating to temperatures of, e.g., 450 to 500 °C so as to form an oxide film of magnetite on the steel surface, aiming at prevention of rusts on the tension mask or reduction of heat radiation, and at this time the tension of the mask sometimes lowers due to creep phenomenon of the steel sheet used to the tension mask. When the tension goes down, an aperture position of the mask may shift, the mask becomes easy
- 20 to be resonated by speaker sound, and an electron beam does not land on a designated position, resulting in so-called "color-deviation".
- [0005] For preventing the creep phenomenon, JP-A-62-249339, (the term "JP-A" referred to herein signifies "Unexamined Japanese Patent Publication"), JP-A-5-311327, JP-A-5-311330, JP-A-5-311331, JP-A-5-311332, JP-A-6-73503, JP-A-8-27541, JP-A-9-296255, and JP-A-11-222628 disclose methods of adding elements such as Mn, Cr,
- 25 Mo to steels for tension masks, or making much N solute in steel sheets for restraining climb motion of dislocation.
- [0006] Further, recently accompanied with cathode ray tubes becoming large scaled, highly defined and flat, other than "color-deviation" caused by creep phenomenon of steel sheets, there has appeared a problem as "color-deviation" also caused by discrepancy in orbits of electron beams due to external magnetic field such as the earth magnetism.
- [0007] For preventing "color-deviation" by the external magnetic field, it is effective to improve the magnetic shielding property of tension masks, and as methods therefore, JP-A-63-145744, JP-A-8-269569 and JP-A-9-256061 show methods of adding Si to steels for tension masks, JP-A-10-219396 shows Cu addition, and JP-A-10-219401 discloses
- 30 Ni addition.
- [0008] However, any investigations have not been made on the magnetic shielding property against external magnetic field in JP-A-62-249339, JP-A-5-311327, JP-A-5-311330, JP-A-5-311331, JP-A-5-311332, JP-A-6-73503, JP-A-8-27541, JP-A-9-296255, and JP-A-11-222628.
- [0009] Besides, the methods described in JP-A-63-145744, JP-A-8-269569, JP-A-9-256061 and JP-A-10-219396 improve the magnetic shielding property, but because of containing Si and Cu, surface defects easily appear on the steel sheet at hot-rolling or recrystallization annealing, and therefore these methods are unwelcome in the application to tension masks requiring severe surface property.
- 40 [0010] The method of JP-A-10-219401 invites cost-up of steel sheets and deteriorates etching property due to the Ni addition.

## DISCLOSURE OF THE INVENTION

- 45 [0011] The object of the present invention is to provide a steel sheet for a tension mask having excellent creep resistance and magnetic shielding property without deteriorating surface property or etching property, a method of making the same, and a tension mask using such a steel sheet.
- [0012] The object of the present invention can be accomplished by a method of making a steel sheet for a tension mask, comprising the steps of: hot rolling a steel containing, by weight %, C: less than 0.1 %, Si: 0.05 % or less, Mn:
- 50 0.4 to 2 %, P: 0.03 % or less, S: 0.03 % or less, sol.Al: 0.01 % or less, N: 0.010 % or more, and the balance being substantially Fe; cold rolling the hot rolled steel sheet; and annealing the cold rolled steel sheet, followed by a secondary cold rolling at a reduction rate of 35 % or higher.

## EMBODIMENTS OF THE INVENTION

- 55 [0013] In general, the magnetic shielding property of steel sheet is evaluated with the permeability thereof, and if decreasing the content of elements in steel such as Mn, Mo, Cr and N, the permeability becomes high, and the magnetic shielding property goes up. However, if decreasing the content of these elements, the creep resistance is deteriorated.

Thus, the improvement of permeability and that of creep resistance tend to be contradictory each other.

[0014] By the way, the cathode ray tube is equipped with a mechanism which supplies current to a demagnetizing coil when turning on an electric source for demagnetizing materials of the tube such as a tension mask. Since this demagnetization is carried out in an external magnetic field, for example, in the earth magnetism, the tension mask is not completely demagnetized but has a residual magnetization. Therefore, for evaluating the magnetic shielding property of the tension mask, an anhysteretic permeability dividing the residual magnetization by the external magnetic field is more preferable than the usual permeability. The higher the anhysteretic permeability, the easier the magnetic flux of external magnetic field, e.g., the earth magnetism passes through the tension mask, and the excellent magnetic shielding property may be obtained.

[0015] As to a steel sheet for a tension mask, we made studies on the relationship between creep phenomenon during the blackening treatment, anhysteretic permeability and color-deviation. As a result, the following findings are obtained.

① If the anhysteretic permeability at a DC bias magnetic field of 0.35 Oe is 3400 or more after blackening treatment, the excellent magnetic shielding property is available, and the color-deviation may be suppressed from a practical view point.

② If Mn of 0.4 % or more and N of 0.010 % or more are added, and the reduction rate of secondary cold rolling after annealing is 35 % or higher, the excellent creep resistance is obtained, and the anhysteretic permeability may be 3400 or more.

③ Adding N of 0.012 % or more, and/or adding Mo in a range of 0.3 % or lower, the creep resistance is further improved.

[0016] The present invention is based on the above findings. The detailed explanation will be made as follows.

#### 1) Chemical composition

[0017] C: This is an element for improving the creeping resistance together with Mn and Mo. An addition of 0.1 % or more precipitates coarse cementites, and deteriorates the etching property. Accordingly, the content of C is set to be less than 0.1 %, preferably 0.06 % or less, and more preferably 0.03 % or less.

[0018] Si: This element forms non-metallic inclusions, and deteriorates the etching property. Accordingly, the content of Si is set to be 0.05 % or less, preferably 0.03 % or less.

[0019] Mn: This is an important element for improving the creep resistance. For providing an excellent creep resistance during the blackening treatment, the content of Mn is set to be 0.4 % or more, preferably exceeding 0.6 %. but although adding more than 2 %, an effect thereby is saturated and a cost-up is invited. Thus, the content of Mn is set to be 2 % or lower.

[0020] P: This is an element causing irregularity in etching, resulting from segregation, and so the content of P is set to be 0.03 % or less, preferably 0.02 % or less.

[0021] S: This is an element unavoidably included in steel. Being more than 0.03 %, it causes hot brittleness and generates etching irregularity. The content of S is therefore set to be 0.03 % or less, preferably 0.02 % or less.

[0022] sol.Al: This is an element which stabilizes solute N as AlN and decreases the said solute N being effective for improving the creep resistance which will be referred to next. Thus, the lesser the better, and the content of sol.Al should be 0.01 % or less.

[0023] N: Making this element solute in steel, it improves the creep resistance. For obtaining an excellent creep resistance during the blackening treatment, its content is necessarily set to be 0.01 % or more. Being 0.012 % or more, the creep elongation is markedly decreased.

[0024] The balance other than the above mentioned composition is substantially Fe.

[0025] In addition to the above composition, if Mo is added in a range of 0.3 % or less, a more excellent creep resistance may be obtained. Mo of more than 0.3 % spoils the etching property.

#### 2) Making method

[0026] The steel containing the above composition in the range of the invention passes, following an ordinary procedure, through smelting - casting - hot rolling - pickling - cold rolling (primary) - recrystallization annealing.

[0027] Subsequently, if performing secondary cold rolling at a reduction of 35 % or more on the above annealed steel sheet, the anhysteretic permeability at a DC bias magnetic field of 0.35 Oe is 3400 or more after the blackening treatment, and therefore the excellent magnetic shielding property may be obtained. This mechanism is not completely cleared, but it may be considered that if the secondary reduction is 35 % or higher, a recovery of the steel sheet easily progresses during the blackening treatment, so that the magnetic property is improved.

[0028] If the reduction rate is considerably increased, not only the anhysteretic permeability is saturated, but also a load of rolling mill increases, and therefore its upper limit is preferably 80 %, and the secondary reduction rate is preferably 40 to 70 %, taking the rolling mill load and the magnetic property into consideration.

[0029] In case there occurs a problem about twist of the grill called as "line disturbance" in the aperture grill, it is preferable to anneal the steel sheet at a temperature range of 450 to 600 °C after the secondary cold rolling for removing residual stress existing in the steel sheet.

[0030] The tension mask made of the steel sheet produced by the method of the present invention has excellent creep resistance and magnetic shielding property, and so this can be sufficient in response to the enlargement, the higher definition and the flattening of cathode ray tubes.

#### EXAMPLE

[0031] The steels A to I in Table 1 were smelted, followed by hot rolling, ground on the surface so as to adjust the sheet thickness, and cold rolled at a reduction rate of 91.3 % to reduce the thickness to 0.14 to 0.5 mm. After the recrystallization annealing, the secondary cold rolling was carried out at a reduction rate of 30 to 80 %, and sample Nos. 1 to 21 of the thickness being 0.1 mm were produced.

Table 1

Steel	C	Si	Mn	P	S	sol.Al	N	Mo	Remark
A	0.0046	0.02	0.45	0.015	0.006	0.005	0.0126	-	Example steel
B	0.0074	0.02	0.40	0.037	0.004	0.005	0.0133	-	Comparative steel
C	0.0081	0.02	0.62	0.008	0.010	0.003	0.0120	-	Example steel
D	0.0071	0.02	0.59	0.007	0.003	0.008	0.0074	-	Comparative steel
E	0.0073	0.02	1.04	0.015	0.005	0.005	0.0148	-	Example steel
F	0.018	0.01	0.61	0.005	0.007	0.008	0.0108	-	Example steel
G	0.150	0.01	0.60	0.007	0.005	0.008	0.0125	-	Comparative steel
H	0.0052	0.02	0.42	0.004	0.035	0.005	0.0123	0.1	Comparative steel
I	0.0057	0.02	0.61	0.015	0.005	0.005	0.0124	0.3	Example steel
Unit: weight %									

[0032] The samples were subjected to the evaluation of etching property, creep resistance, and magnetic property through the following manners.

[0033] As to the etching property, the aperture grill was subjected to the actual etching like a blind screen for visual evaluation of defects. ○ denoted the case when no defect was present, and × denoted the case when any defect was present.

[0034] As to the samples of the good evaluation in the etching property, the creep resistance and the magnetic property were evaluated.

[0035] As to the creep resistance, the samples were held at 450 °C for 20 minutes under a condition of loading tension of 300 N/mm<sup>2</sup>, and ⊙ denoted the especially good case of the creep elongation being 0.40 % or less, ○ denoted the case when the creep elongation being above 0.40 % but below 0.60 %, and × denoted the case of the creep elongation exceeding 0.60 %, as not durable case to use. By the way, the creep elongation was an average value in the rolling direction and in the right angled direction to the rolling.

[0036] As to the magnetic property, the samples were subjected to the heating treatment at 450 °C for 20 minutes corresponding to the blackening treatment, and from these treated samples, taken out were ring test pieces of the outer diameter being 45 mm and the inner diameter being 33 mm, on which a magnetizing coil, a search coil, and a DC-bias-field coil were set for measuring the permeability ( $\mu$  0.35) at 0.35 Oe, the residual magnetic flux (Br) at the maximum magnetizing field being 50 Oe, the coercive force (Hc), and the anhysteretic permeability. The anhysteretic permeability was measured in the following way.

① The damping AD current was supplied to the magnetizing coil to completely demagnetize the test pieces.

② The DC current was supplied to the DC-bias-field coil to generate the DC bias magnetic field being 0.35 Oe, and under this condition, the damping AD current was again supplied to the magnetizing coil to demagnetize the test pieces.

## EP 1 170 388 A1

③ The DC current was supplied to the magnetizing coil to magnetize the test pieces, and the generated magnetic flux was detected by the search coil for measuring B-H curve.

④ The anhysteretic permeability was calculated from the B-H curve.

5 [0037] The results are shown in Table 2.

[0038] In the examples Nos. 1, 4 to 8, 13 to 16 and 19 to 21, the etching property and the creep resistance were good, and the anhysteretic permeability was 3400 or more and the magnetic shielding property was excellent. In particular, as to the creep elongation, in case N was 0.010 % or more, it went down to 0.60 % or less, and in case N was 0.012 % or more, or Mo was added, the creep resistance was good. If the secondary reduction rate was 35 % or more, the anhysteretic permeability was above 3400.

10 [0039] On the other hand, in the comparative examples Nos. 2, 3, 9 to 12, 17 and 18, one or more of the etching property, the creep resistance and the magnetic property were inferior.

15

20

25

30

35

40

45

50

55

Table 2

Sample No.	Steel	Secondary reduction rate (%)	Etching property	Creep resistance		Magnetic property				Remarks
				Elongation (%)	Evaluation	$\mu$ 0.35	Br(G)	Hc(Oe)	Anhyseretic permeability	
1	A	50	○	0.53	○	170	10400	6.2	4250	E
2	B	60	×	—	—	—	—	—	—	C
3	C	30	○	0.47	○	170	8200	6.7	3380	C
4	C	35	○	0.48	○	170	9000	6.7	3720	E
5	C	40	○	0.50	○	170	9700	6.7	4000	E
6	C	60	○	0.58	○	170	10700	6.7	4380	E
7	C	70	○	0.58	○	170	10700	6.7	4400	E
8	C	80	○	0.60	○	170	10700	6.7	4400	E
9	D	35	○	0.63	×	175	9300	6.7	4100	C
10	D	50	○	0.65	×	175	10800	6.7	4760	C
11	D	60	○	0.76	×	175	11000	6.7	4840	C
12	E	30	○	0.27	⊙	165	8100	7.6	3160	C
13	E	35	○	0.28	⊙	165	8900	7.6	3480	E
14	E	50	○	0.28	⊙	165	10300	7.6	4030	E
15	E	70	○	0.33	⊙	165	10500	7.6	4120	E
16	F	60	○	0.52	○	170	10700	7.0	4500	E
17	G	50	×	—	—	—	—	—	—	C
18	H	60	×	—	—	—	—	—	—	C
19	I	35	○	0.37	⊙	170	9000	6.6	3680	E
20	I	50	○	0.39	⊙	170	10400	6.6	4270	E
21	I	60	○	0.45	○	170	10600	6.6	4340	E

E: Example

C: Comparative example

## Claims

1. A method of making a steel sheet for a tension mask, comprising the steps of:

hot rolling a steel containing, by weight %, C: less than 0.1 %, Si: 0.05 % or less, Mn: 0.4 to 2 %, P: 0.03 %

**EP 1 170 388 A1**

or less, S: 0.03 % or less, sol.Al: 0.01 % or less, N: 0.010 % or more, and the balance being substantially Fe;  
cold rolling the hot rolled steel sheet; and  
annealing the cold rolled steel sheet, followed by a secondary cold rolling at a reduction rate of 35 % or higher.

- 5     2. The method as set forth in claim 1, using a steel containing N: 0.012 % or more.
3. The method as set forth in claim 1, using a steel further containing Mo: 0.3 % or less.
- 10    4. The method as set forth in claim 2, using a steel further containing Mo: 0.3 % or less.
5. A steel sheet for the tension mask produced by the method as set forth in any one of claims 1 to 4.
6. A tension mask, using the steel sheet as set forth in claim 5.

15

20

25

30

35

40

45

50

55

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/08984

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int.Cl. <sup>7</sup> C21D9/46, C22C38/00, 38/06, 38/12, H01J29/07		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int.Cl. <sup>7</sup> C21D9/46-48, C22C38/00-60, H01J29/07		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2001 Kokai Jitsuyo Shinan Koho 1971-2001 Jitsuyo Shinan Toroku Koho 1996-2001		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 8-27541, A (Nisshin Steel Co., Ltd.), 30 January, 1996 (30.01.96), tables 1,2 (Family: none)	1-6
X	JP, 9-227998, A (Nisshin Steel Co., Ltd.), 02 September, 1997 (02.09.97), tables 1,2 (Family: none)	1-6
A	GB, 2334140, A (DAINIPPON PRINTING CO LTD, TOYO KOHAN CO LTD), 11 August, 1999 (11.08.99) & JP, 11222628, A & DE, 19904792, A1 & CN, 1237778, A & KR, 99072445, A	1-6
A	JP, 5-311330, A (NKK Corporation, Nippon Mining & Metals Company, Ltd.), 22 November, 1993 (22.11.93) (Family: none)	1-6
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 08 March, 2001 (08.03.01)		Date of mailing of the international search report 21 March, 2001 (21.03.01)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)